Effect of Processing Parameters on the Mechanical Properties of *In Situ* Compatibilized Polybutylene Terephthalate/Acrylonitrile–Butadiene–Styrene Blends

José Donato Ambrósio,[1]   **Elias Hage Junior**[2]

[1]*Center for Characterization and Development of Materials, Federal University of São Carlos, CP 388, São Carlos-SP, 13.565-970, Brazil*
[2]*Department of Materials Engineering, Federal University of São Carlos, Via Washington Luiz km 235, São Carlos-SP, 13.565-905, Brazil*

ABSTRACT: To evaluate mechanical properties of blends prepared by intermeshing corotating twin-screw extrusion (ICTSE), it is usually necessary to injection mold specimens after the extrusion mixing process. At this study an alternative method is used to obtain testing specimens from ribbons extruded polybutylene terephthalate/acrylonitrile–butadiene–styrene blends, (PBT/ABS), compatibilized with methyl methacrylate–glycidyl methacrylate-ethyl acrylate (MGE) by ICTSE, and then to correlate their mechanical properties with the processing parameters. Regarding to the extrusion process parameters, it has been noted that higher feed rates, lower screw speeds and narrower kneading blocks have reduced the ductile-brittle transition temperature (DBTT) of the compatibilized PBT/ABS blends, thereby suggesting that the molecule integrity of blend polymeric components has been preserved and that a good dispersion of the ABS domains in the PBT matrix has been achieved. Injection molded PBT/ABS blends were obtained to compare to the extruded ribbons. The mechanical tests for both specimens have shown the same trends. The injection molded samples have presented poorer impact strength, tensile strain at break and tensile strength, when compared to the respective extruded samples. That behavior has been attributed to the high level of molecular orientation resulting from the injection molding process and mainly to PBT degradation during process. The PBT degradation could have increased its degree of crystallinity, which has been confirmed by DSC measurements. As result, the blend became more brittle, decreasing its Izod impact strength. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2753–2765, 2012

Key words: intermeshing corotating twin-screw extruder; PBT/ABS blend; extrusion dies; mechanical properties; injection molding; crystallization

INTRODUCTION

The intermeshing corotating twin-screw extrusion (ICTSE) is one of the main processes to compound polymer blends. The twin-screw extruder may have interchangeable screw elements to promote better mixing. However, the modulated twin-screw extruder lead to quite complex mixing process mechanisms. It is probably the most complex of the commercial machines involving several different types of elements, which are closely intermeshing and self-wiping.[1] According to Todd,[2] the breadth of this success can, to a significant extent, be attributed to the machine's flexibility, which allows it to be set up in almost infinite number of mechanical configurations and operating conditions. However, the flexibility one has in specifying process variables is what separates twin-screw extrusion processing from all the others. Therefore, each unit operation must be equated to the most effective set of process parameters, taking into account upstream and downstream boundary conditions.

A wide range of techniques has been developed to follow-up the blend morphologies of blends along extruder barrel and extruder dies has been reported. However, just a few of them correlate processing parameters in an ICTSE and mechanical properties of blends. Some of those experimental techniques have been mentioned.[3–10]

Oosterlinck et al.[3] have monitored the processing of poly(methyl methacrylate)/polystyrene blends (PMMA/PS) and have pointed out that at the extrusion die inlet region the particles of the disperse phase, originally spherical, have its shape altered primarily to a fibril shape and finally to the spherical shape once more, depending on the shearing background and on the radial position in the

extrusion die. Yichong and Fuhua[4] have installed glass windows on the sides of the extruder barrel and on the screw intermeshing region. A blend of high impact polystyrene and low-density polyethylene has been processed and it has been observed that the filling of the screw channels is influenced by feed rate, screw speed, screw geometry, degree of positive displacement of the material, and material properties. Carneiro et al.[5] have studied the influence of processing parameters, such as, screw speed, feed rate, barrel temperature, and screw geometry on the pressure, temperature and residence time of polypropylene (PP) extruded by ICTSE. Six points along the barrel and one point at the extrusion head were chosen to observe the morphology. Experimental and numerical data obtained from the *Ludovic software* were compared showing that not only the screw geometry, with different conveying elements and kneading blocks configurations, but also and mainly the processing parameters have affected significantly the pressure, temperature, and residence time of PP extruded. Yang[6] has evaluated the influence of viscosity ratio and temperature on the morphology of polycarbonate (PC) and acrylonitrile–butadiene–styrene (ABS) blend using a method based on the emergency stop of the extruder followed by quenching and removal of the screw to analyze the material contained in the screw channels. Scanning electron microscopy (SEM) has revealed that plotting the average particle size of the ABS disperse phase as a function of the viscosity ratio (η_{ABS}/η_{PC}) results in a concave curve with the minimum when the viscosity ratio is close to the unity.

Employing also the method above described, Potente et al.[7] have blended PP and polyamide 6 (PA6) in 25.0 and 40.0 mm diameter extruders, concentrating the kneading blocks at the end of the screw. It has been seen that the average particle size of the PA6 phase has not experienced significant changes along the kneading blocks region. Samples taken from the end of the kneading blocks region led to a more prominent decrease on PA6 average particle size has occurred, probably due to the viscosity ratio, which is close to one. No influence of the extruder diameter (25 or 40 mm) on the average particle size and particle size distribution has been observed. Huneault et al.[8] have collected samples of polyethylene/polystyrene blends with the extruder still in operation. To investigate polyethylene disperse phase, the samples have been immersed in tetrahydrofuran to solubilize the polystyrene matrix and filtered to separate the polyethylene. SEM has shown a fibril disperse phase, typical of regions with low shear rate. Spherical particles would probably be observed if the samples had been taken form regions subjected to high shear rates. Another conclusion was that increasing the thickness of the

kneading blocks, a reduction on the recirculation of the material within the screw channels took place. However, the absolute shear rate has been increased.

Shearer and Tzoganakis[9,10] have called upon interfacial reaction between two polymeric tracers to investigate the efficiency of the distributive mixing in twin-screw extrusion. It has been found out that the efficacy of distributive mixing depends on the amount of molten material along the kneading blocks. When the channels of the kneading blocks were totally filled with polymeric material and using slower screw speeds, the degree of reaction observed was higher for both reverse and neutral flow kneading blocks, probably due to the stagnation of the molten material.

The PBT/ABS blend has been initially studied by Hage et al.[11] to verify the influence of ABS type and blend composition on blend morphology and impact strength. With the addition of at least 30 wt %, all three ABS types used, containing different amounts of the elastomeric phase (polybutadiene), have enhanced the notched Izod impact strength of PBT. However, the blends showed unstable morphologies, since at quiescent melt conditions the ABS domains coalesce, what leads to a worsening of the impact properties. Attempting to improve the restricted compatibility of the polymers PBT and ABS, Hale et al.[12–14] have synthesized a terpolymer composed of methyl methacrylate (MMA), glycidyl methacrylate (GMA), and ethyl acrylate (EA), resulting in the terpolymer known as MGE. Evidences of chemical reaction between the PBT polymer chain end groups, that is, hydroxyl and carboxyl groups, and the epoxy functional groups of the GMA present in the MGE have been observed, originating the graft copolymer PBT-*g*-MGE. Mantovani[15] has also worked with different ABS types to study toughening of PBT/ABS. Blends with high impact strength at room temperature have been reported and the best results have been achieved with the ABS containing the smallest content of emulsifiers residues. Moreover, the MGE has stabilized the blend morphology, as confirmed by transmission electron microscopy. Canto et al.[16] studied the development of the phase morphology in uncompatibilized PBT/ABS and *in situ* compatibilized PBT/ABS blends during compounding in a twin-screw extruder. For both blends, significant refinement on the phase morphology was found to occur after the blends pass through the extruder die, and this phenomenon was correlated to the capacity of the die in promoting particles break-up due to the extra elongational stresses developed at the extruder die entrance.

There are several studies of other compatibilizers used for the blend PBT/ABS. Yao et al.[17] compatibilized the PBT/ABS blends with a copolymer of styrene–acrylonitrile–maleic anhydride (ASMA) and

epoxy resin, and observed by means of comparative analysis of the morphology and rheological properties, that epoxy resin can be a coupling agent, which leads to the formation of ASMA-EP-PBT grafted copolymers, which gets compatibilized the blend. Sun et al.[18] compatibilized the blend PBT/ABS with styrene–acrylonitrile glycidyl methacrylate (SAG) copolymer, and found that the SAG was miscible in the SAN and could react with carboxyl and hydroxyl groups of PBT, the effect being the compatibility confirmed by analysis of morphological, rheological, and mechanical properties.

Despite the PBT/ABS blends studied so far presented very attractive performance for impact strength behavior, there is still a lack of studies concerning how these properties are affected by the extrusion parameters, like extrusion feed rate, screw speed and geometry of the kneading blocks of the screw.[19] Thus, the aim of this study was to develop a different procedure by designing and manufacturing devices for an ICTSE, to correlate the processing parameters involved in the compounding of PBT/ABS and mechanical properties of the blend, such as Izod impact strength and tensile properties; comparing results obtained for the extruded ribbons samples and for the same samples injection molded after the extrusion.

EXPERIMENTAL

Materials

The materials used as blends constituents were the polybutylene terephthalate (PBT) and the ABS terpolymer, commercially known as Valox 315 and Cycolac 36360, respectively. This PBT has a melt flow index of 6.3 g/10 min when measured at 250°C under a load of 1.20 Kg, and its average numerical molar mass measured by viscosimetry is 42,000 g/mol.[20] ABS obtained by emulsion polymerization was quantitatively characterized by Fourier transform infrared spectrometry and presented 51 wt % butadiene, 36 wt % styrene, and 13 wt % acrylonitrile.[19] Both materials have been provided by Sabic Innovative Plastics South America. The MGE terpolymer, used as the compatibilizing agent synthesized by bulk copolymerization with the following composition MMA (88 wt %), GMA (10 wt %), and EA (2 wt %).

Capillary rheometry testing

The capillary rheometry analyses have been performed at 250 and 275°C, with a 0.381 mm radius (R_c) and $L_c/(2R_c) = 33$ capillary die, and shear rates ranging from 100 to 10,000 s^{-1} have been used. Initially, all the blends were prepared in a HAAKE tor-

que rheometer with 60 rpm at 250°C. After that, the blend has been milled and measurements using a capillary rheometer have been performed. The pressure drop (ΔP) values obtained from the capillary rheometry for different flow rates (Q) for the molten blend, was initially plotted as log ($\Delta P R_c/2L_c$) versus log ($4Q/\pi R_c^3$). Assuming that the non-Newtonian behavior for molten blend follows a power-law relation, it was obtained by linear regression a straight line whose intercept and slope provided the values of consistency (m) and the power law index (n), respectively. The corrected shear rate ($\dot{\gamma}_{corr}$) in the capillary die wall was obtained by eq. (1) and the corrected viscosity (η_{corr}) by eq. (2).[21] With those values, it was then plotted a graph of log $\dot{\gamma}_{corr}$ versus log η_{corr} for the neat polymers and for binary PBT/ABS and *in situ* compatibilized PBT/ABS/MGE blends.

$$\dot{\gamma}_{corr} = \left(\frac{3n+1}{4n}\right)\left(\frac{4Q}{\pi R_C^3}\right) \qquad (1)$$

$$\eta_{corr} = m(\dot{\gamma}_{corr})^{n-1} \qquad (2)$$

Blends preparation

The blends were mixed in a 30 mm diameter and $L/D = 35$ Werner-Pfleiderer ICTSE using two screw profiles as shown in Figure 1. Both of them exhibit two kneading blocks type KB45/5/42 at the fourth barrel of the extruder, to melt PBT before the addition of ABS and MGE on the fifth barrel of the extruder through a side feeder. The PBT was in the form of pellets, while ABS and MGE in the form of powder. The four kneading blocks type KB45/5/42 or KB45/5/14 located at the end of the screw are responsible for the mixing of blends components. Besides that, three pressure transducers, two of them were fixed right before and after the four kneading blocks, DPe and DPs, respectively, and another one was located at the extrusion die inlet (DPc). The uncompatibilized and compatibilized blends have been prepared on the proportions of PBT/ABS (70/30) and PBT/ABS/MGE (65/30/5), respectively. The thermal profile along the extruder was 260/270/240/240/240°C and the temperature at the die head was 240°C. The pressure, torque, and melt temperature at the die outlet have been monitored. The extrusion head with extrusion dies has been designed considering a maximum pressure of 9,653 kPa at the extrusion head inlet.[22]

To estimate the pressure drop along the extrusion head,[23,24] eq. (3) has been employed.

$$\Delta P = \left(\frac{2\text{ mL}}{H}\right)\left(\frac{2Q(1+2n)}{nWH^2}\right)^n \qquad (3)$$
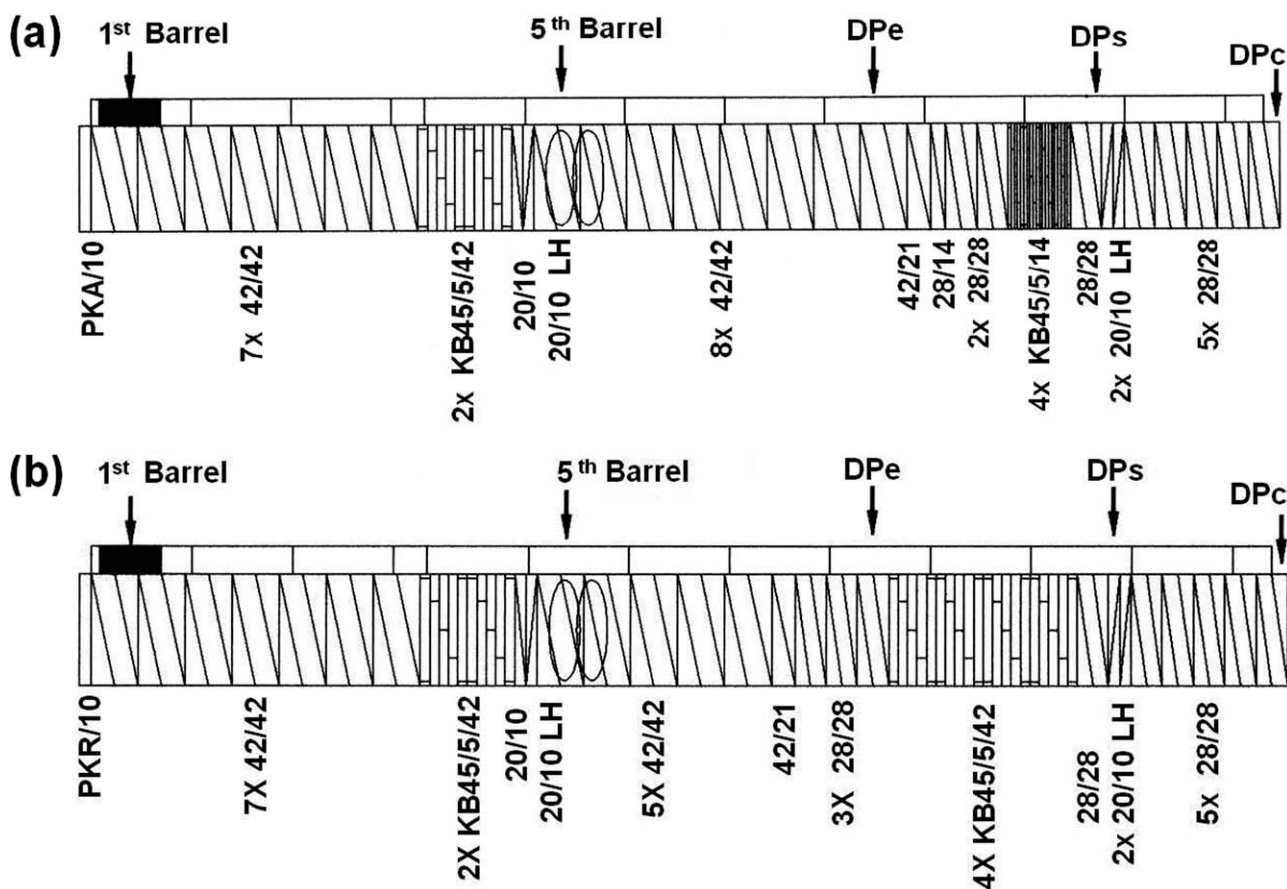
Figure 1 Screw geometry configurations with pressure transducers located before and after the four kneading blocks (DPe and DPs) and at the extrusion die inlet (DPc). (a) Screw type 4KB45/5/14 and (b) Screw type 4KB45/5/42.

where ΔP is the pressure drop, L is the extrusion die length, W is the extrusion die width, H is the extrusion die height, Q is the flow rate, n is the power law index, and m is the consistency.

To compare the mechanical properties extruded ribbons 25.0 mm wide and 3.6 mm thick has been used as specimens after machining, as well as, injection molded specimens were prepared using an 30 ton Arburg, model 270, injection molding machine. The ribbons have been milled prior to the injection molding. The samples have been injection molded under the following conditions: thermal profile of 230/240/240/240/255°C, injection speed 40 cm^3/s, packing pressure 450 bar/10 s, back pressure 60 bar, mold temperature 50°C, and cooling time 30 s. Before injection, all the samples have been dried for 8 h at 60°C.

Mechanical testing

Test specimens for notched Izod impact strength and tensile stress tests, according to ASTM D256-2002 and ASTM D638-2003 (test specimen type V), respectively, have been taken directly from the extruded ribbons and also injection molded. The

specimens for tensile tests and impact strength, obtained from the extruded ribbons, were machined through the longitudinal direction of the extruded ribbons, allowing specimens 25.0 mm wide and 3.6 mm thick. The depth under the notch of the specimen is 10.2 mm. For each sample were tested 10 specimens in the temperature range from -80 to 20°C with intervals of 10°C. The tensile tests were done for each six specimens at 25°C and a crosshead speed of 10 mm/min.

Differential scanning calorimetry (DSC)

The samples of the PBT/ABS blend have been thermally characterized by Differential Scanning Calorimetry (DSC), using a Mettler-Toledo DSC, model 822^e, after extrusion and injection molding processes. The DSC curves were obtained using a closed aluminum pan and a nitrogen atmosphere. The blend samples were first heated up to 250°C, followed by cooling down to 30°C temperature and then reheated up to 250°C, at heating and cooling rates of 10 and -10°C/min, respectively. With the first and second heating, the melting temperatures T_{m1} and T_{m2}, and the enthalpy of fusion $\Delta H1$ and $\Delta H2$ have
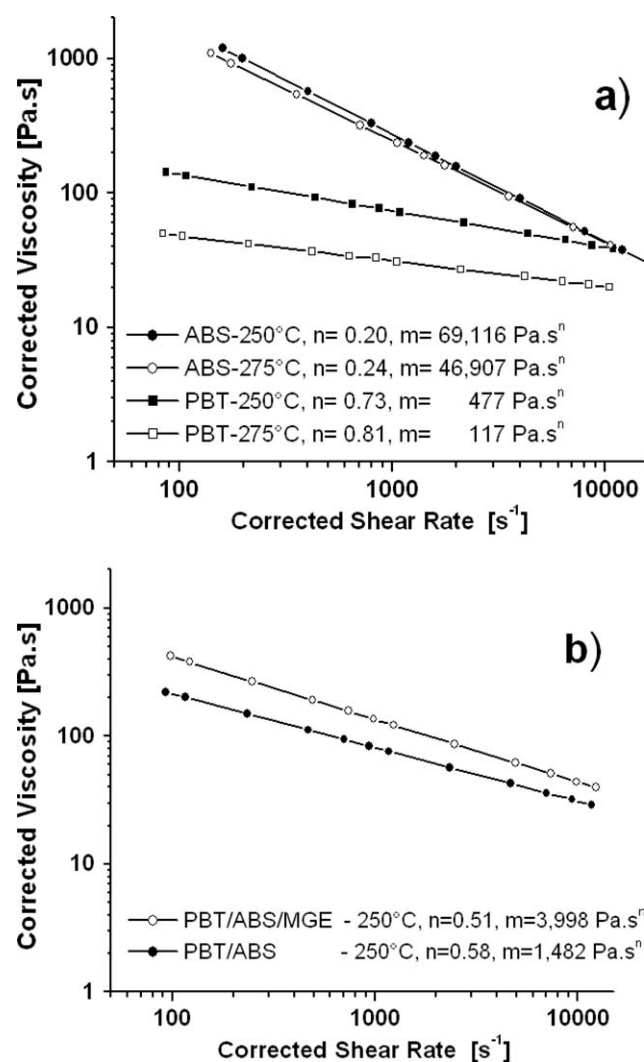
Figure 2 Corrected viscosity versus corrected shear rate curves and values of m and n. (a) PBT and ABS and (b) PBT/ABS and *in situ* compatibilized PBT/ABS/MGE blends.

been determined, while during cooling the crystallization temperature (T_c) and the enthalpy of crystallization (ΔHc) have been measured. All the measured cooling and heating enthalpies were calculated based only in the PBT phase content.

RESULTS AND DISCUSSION

Capillary rheometry analysis

Corrected viscosity versus corrected shear rate curves, according to the power-law relation,[21] for neat PBT, neat ABS, PBT/ABS, and also *in situ* compatibilized PBT/ABS blends, at two different temperatures are presented in Figure 2. Regarding the influence of the temperature on the viscosity, it can be said from Figure 2(a) that PBT's viscosity is highly sensitive to changes in temperature. A difference of 25°C, that is, from 250 to 275°C, was enough

to drop the viscosity from 150 to 50 Pa.s, in shear rates of 100 s^{-1}, and from 40 to 20 Pa.s in shear rates of 10,000 s^{-1}. However, the viscosity of the ABS terpolymer is not severely affected by changes in temperature within the shear rate range studied. In addition, the temperature plays not a significant role on the ABS viscosity for shear rates higher than 3,000 s^{-1}.

Concerning the PBT and ABS viscoelastic properties, one can note from Figure 2(a) that the consistency parameter (m), which corresponds to the shear stress when the shear rate is extrapolated to 1 s^{-1}, is quite distinct for both materials. While for PBT the m values are 477 Pa.s^n at 250°C and 117 Pa.s^n at 275°C, for ABS the m values are 69,116 and 46,907 Pa.s^n, respectively, that is, a difference of two orders of magnitude. The high value of m for ABS is expected for polymers with high rubber content. The power law index (n) was 0.73 at 250°C and 0.81 at 275°C for PBT and 0.20 and 0.24 for ABS, respectively. Those values demonstrate that PBT shows a trend to be a Newtonian fluid, while ABS has a strong pseudoplastic behavior. The considerations above are really important to comprehend that during the processing in an ICTSE the important variables to decrease PBT viscosity are adiabatic heat from the drag flow and conductive heat from the extrusion barrel.[25] To reduce ABS viscosity the main factor to be considered is the shear rate, since the last is just slightly sensitive to changes in temperature.

Sample of the *in situ* compatibilized PBT/ABS blend have exhibited viscosities nearly 2.5 times higher than the PBT/ABS binary blend. This can be a consequence of an increase on the molecular weight of the *in situ* compatibilized PBT/ABS blend due to the presence of graft copolymer PBT-*g*-MGE, which could interfere on the flow of the molten material. Smaller particle size of the ABS disperse phase, due to the *in situ* compatibilization and a better distribution of them within the PBT matrix could also difficult the flow by increasing the interfacial area in the blend.

PBT/ABS extrusion

The side view design and a picture of the extrusion head and extruded ribbon are illustrated in Figure 3. As presented in Figure 3(a), the design of the extrusion head allows the use of extrusion dies with different cross sections and lengths.

The standard extrusion die was 2.0 mm long to eliminate possible influences of die length on the mechanical properties of all six samples obtained, as showed in Table I. Only one sample has been processed with the 62.0 mm long extrusion die, to evaluate the effect of the extrusion die length on the
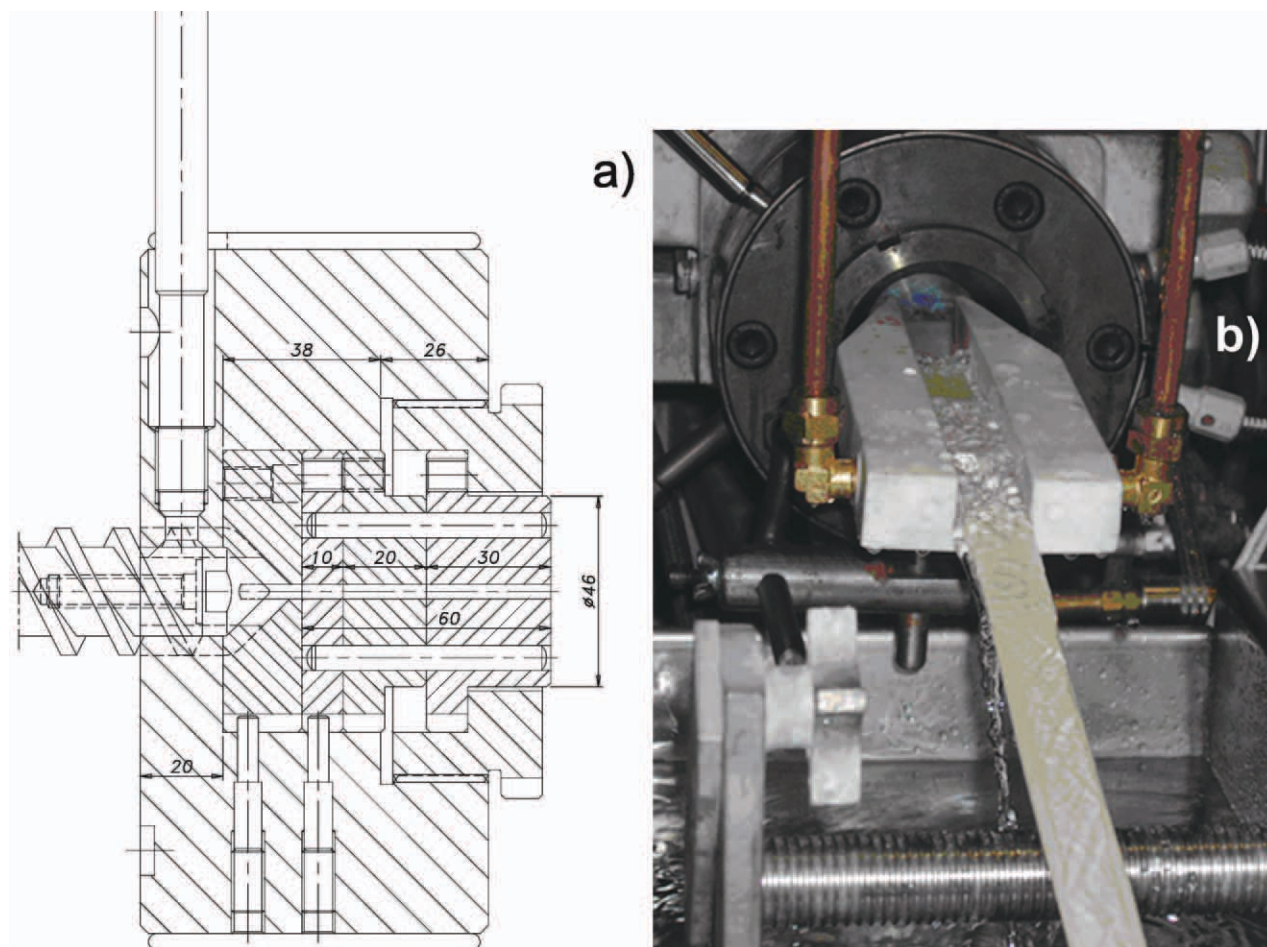
Figure 3 Intermeshing corotating twin-screw extruder head. (a) Extrusion head side view and (b) Ribbon being pulled through the mini channel apparatus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanical properties of the blend; and to compare the pressure drop along the extrusion head determined with eq. (3) and the experimental data recorded during the extrusion. Figure 3(b) presents a mini-channel apparatus, which has been positioned at the end of the extrusion line to help cooling of the extruded ribbon.

The experimental design showed in Table I present the selected five processing parameters. The effect of each one of these parameters on the mechanical properties, that is, the impact behavior and tensile stress properties of PBT/ABS blends has been analyzed. Sample BD01 is the reference for all the other five samples, which differ from the sample BD01 by only one process parameter. In addition to the experimental design parameters shown in Table I, relevant operational aspects of the twin screw extruder, such as motor torque, melt temperature and pressure (DPe, DPs, and DPc) have also been monitored throughout the compounding of the samples, as indicated in Table II. The torque values,

expressed in percentage, are proportional to the maximum torque of the extruder, which is 180 Nm.

For all the samples, the pressure transducer located before the kneading blocks (DPe) has not registered any pressure, suggesting that the four kneading blocks were not fully filled with molten material. As noted from Table II, a comparison of samples BD02, a binary PBT/ABS blend, and BD01,

TABLE I
Extrusion Processing Parameters

		Extrusion processing parameters			
Sample	MGE (% wt)	Feed Rate (kg/h)	Screw Speed (rpm)	Die Length (mm)	Screw
BD01	5	7.0	120	2.0	4KB45/5/42
BD02	0	7.0	120	2.0	4KB45/5/42
BD03	5	3.5	120	2.0	4KB45/5/42
BD04	5	7.0	240	2.0	4KB45/5/42
BD05	5	7.0	120	62.0	4KB45/5/42
BD06	5	7.0	120	2.0	4KB45/5/14

TABLE II
Operational Aspects Monitored During the Compounding of the Blends

Sample	Motor torque (%)	Molten temperature (°C)	DPs (kPa)	DPc (kPa)
BD01	86	256	738	97
BD02	77	256	427	55
BD03	69	249	427	62
BD04	86	270	531	62
BD05	89	261	572	1096
BD06	83	265	717	76

a ternary PBT/ABS/MGE blend with 5 wt % MGE, reveals an increase of 15% on the torque, suggesting a higher viscosity for the ternary blend, probably as a consequence of chemical reaction between MGE and carboxylic/hydroxylic groups from PBT. The torque of 86%, observed for BD01, was one of the limiting factors that led to a maximum feed rate of 7.0 kg/h. Values of pressure after the four kneading blocks (DPs) and at the extrusion head inlet (DPc), as indicated in Figure 1, are higher for the compatibilized blend (BD01) than for the uncompatibilized blend (BD02). This also indicates reactivity between PBT and MGE.

The torque measured for sample BD03, blended with a feed rate of 3.5 kg/h, happens to be significantly smaller than the one recorded for sample BD01, processed with 7.0 kg/h. This could mean that the screw channels were not fully filled, demanding less effort of the machine motor. Molten temperature, DPs and DPe have also decreased with the feed rate used for BD03, that is, 3.5 kg/h.

The screw speed has also affected molten temperature. Sample BD04, processed with 240 rpm, has presented a molten temperature 14°C higher than sample BD01, which has been prepared with 120 rpm. The elevation of the molten temperature caused by faster screw speeds has already been noted by Carneiro et al.[5] in studies with PP. The faster the screw speed, the higher the shearing, what can have generated extra heat. Thus, the reduction of the pressure at extrusion head inlet can be a reflex of a decrease on the blend viscosity.

As previously mentioned, an extrusion die as short as possible, that is, 2.0 mm long, has been adopted as the standard to minimize its effects on the residence time and to prevent high levels of molecular orientation, what would interfere on the evaluation of the mechanical properties. An increase from 2.0 to 62.0 mm, or from BD01 to BD05, had a significant influence on the pressure at extrusion head inlet (DPc), as indicated in Table II. The pressure has jumped from 97 kPa, 2.0 mm long die (BD01), to 1,096 kPa, 62.0 mm long die (BD05). That change is related to the flow resistance imposed by the extrusion die. In addition, the resistance to flow could lead to higher residence time, higher melt temperature, and higher torque, as shown in the Table II.

From the sample BD05 in Table II, it is possible to compare the experimental pressure measured at the extrusion head inlet with a simulated value, as described as follows. By applying eq. (3), and using extrusion die geometry, such as, $L = 62.0$ mm, $W = 25.0$ mm, and $H = 3.6$ mm, a feed rate of 7.0 kg/h and considering that $n = 0.51$ and $m = 3,998$ Pa.s^n, for the *in situ* compatibilized PBT/ABS blend, a pressure of 958 kPa was obtained. Therefore, experimental (1,096 kPa) and calculated (958 kPa) values are relatively close to each other and the difference verified can be the result of several factors, such as, differences in temperature, approximations arising from the use of the power-law and the position of the pressure transducer, which was not exactly at the extrusion die inlet, but slightly before. Summarizing, the use of the power-law relation together with rheological properties from a capillary rheometer, can be an important tool for estimating pressure drop along extrusion die heads, providing reliable values.

PBT/ABS blends mechanical behavior

A change in impact strength behavior by changing the temperature can be used to determine the existence of ductile-brittle transitions or alternatively the susceptibility of polymeric materials to stress concentration. An important property when dealing with toughening of blends is the ductile-brittle transition temperature (DBTT) that is defined as the average temperature from which an accentuated drop on the impact strength due to change in the temperature is observed.[26] Figure 4 shows the criterion used to estimate the DBTT for the BD01 sample. To
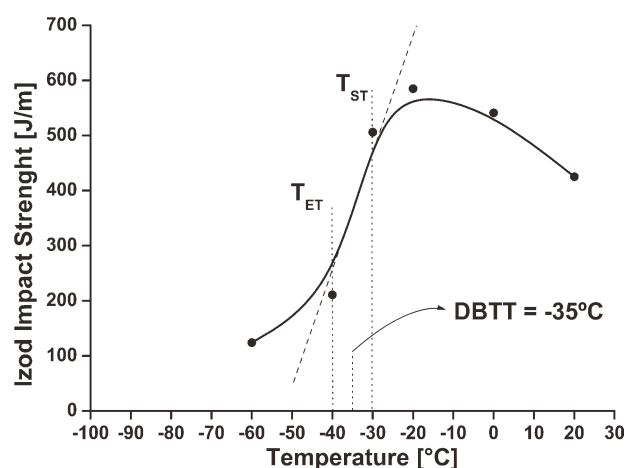
Figure 4 Notched Izod impact strength curve as a function of temperature for BD01 sample showing DBTT.
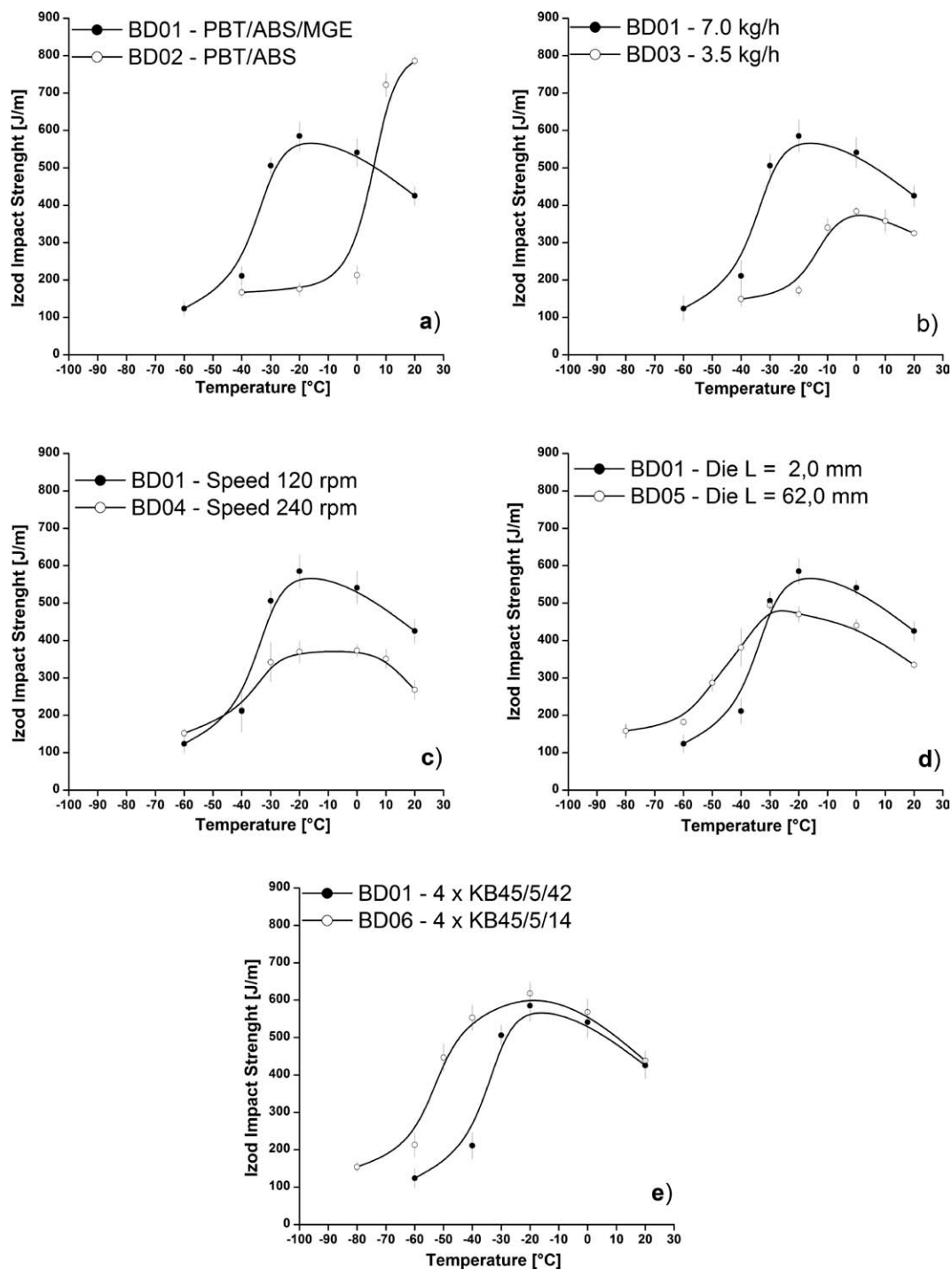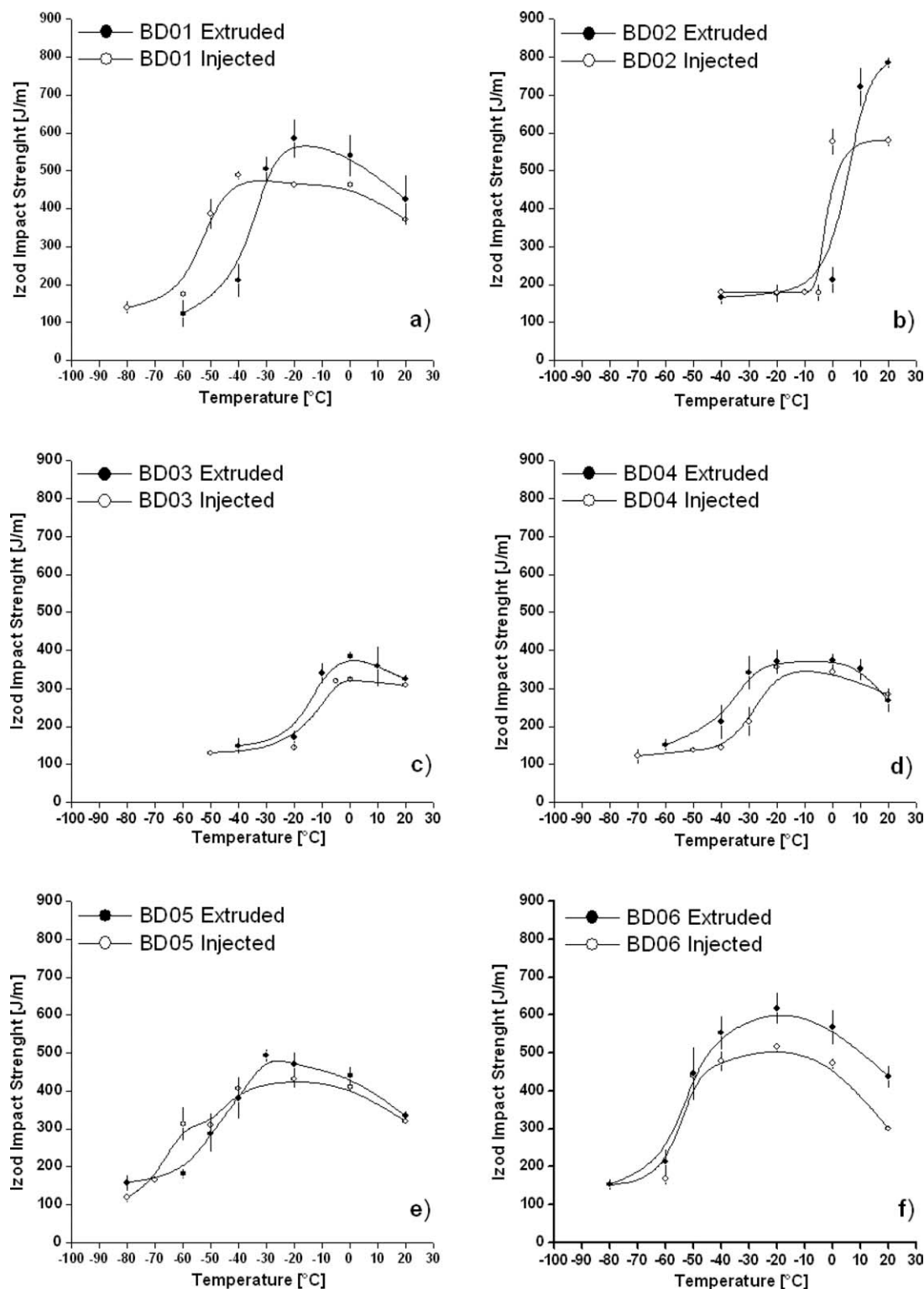
Figure 5 Notched Izod impact strength as a function of temperature for PBT/ABS blends processed in different conditions. (a) Presence of the compatibilizer MGE, (b) feed rate, (c) screw speed, (d) extrusion die length, and (e) type of kneading blocks.

estimate the DBTT was drawn a straight line through the two close temperatures that showed the greatest difference in impact strength, where T_{ST} was considered the onset temperature of ductile-brittle transition and T_{ET} the ended of ductile-brittle transition. So the DBTT was estimated as an average temperature between T_{ST} and T_{ET}.

The impact behavior of the PBT/ABS blends, by using test specimens taken directly from the extruded ribbons, are shown through Figures 5 and 6 and in Table III. In Figure 5(a) and in Table III, the presence of MGE has decreased the DBTT from 5°C for extruded BD02 to −35°C for extruded BD01. The glass transition temperature (T_g) for PBT Valox 315

Figure 6 Curves comparing the notched Izod impact strength as a function of temperature of extruded and injection molded PBT/ABS blends, under different processing parameters.

is 50°C, and for polybutadiene component of ABS is −85°C.[19] Probably the MGE has refined blend morphology, preventing coalescence of ABS particles and maintaining an adequate distribution of ABS particles within the PBT matrix.[11–14] This correlation between the decrease of DBTT and increase of ABS dispersion can be explained by considering that the increase of ABS dispersion means a large reduction of the average surface-to-surface rubber interparticle distance.[27]

TABLE III
Impact Strength at 20°C and Ductile-Brittle Transition Temperature (DBTT) of Extruded and Injection Molded PBT/ABS Blends

Sample	Impact strength at 20°C		DBTT	
	Extruded (J/m)	Inj. Molded (J/m)	Extruded (°C)	Inj. Molded (°C)
BD01	425	372	−35	−55
BD02	790	580	5	0
BD03	315	309	−15	−10
BD04	268	284	−35	−30
BD05	335	320	−45	−55
BD06	438	301	−55	−55

From Figure 5(b) and in Table III, it can be verified that higher feed rates have increased the impact strength at room temperature and decreased the DBTT. The impact strength, as well as, the DBTT has been severely compromised by the feed rate of 3.5 kg/h. Moreover, the DBTT values are close to the ones obtained for the non compatibilized blend. This could be a consequence of the degradation of blends constituents, caused by elevated residence times for the lower feed rate. Once the screw channels were not completely filled with molten material, there would not be enough pressure to push the blend forward.

The sample processed with 120 rpm (BD01) has exhibited higher Izod impact strength than the ones prepared with 240 rpm (BD04), as indicated by Figure 5(c). This can also be related to the degradation of blends constituents, as suggested by the melt temperatures of Table II, which is significant high for both PBT and ABS. The melt temperatures recorded for 240 rpm and for 120 rpm were 270 and 256°C, respectively. In addition, the shearing arising from the kneading blocks at 240 rpm would be nearly two times the shearing at 120 rpm,[28] which can lead to higher melt temperatures.

By using the 62.0 mm long extrusion die (BD05), it has decreased the impact strength of the PBT/ABS blend, as revealed by the curves of Figure 5(d). The longer the extrusion die, the larger the resistance to flow and, therefore, the material can have stayed longer in the machine, increasing the residence time for the blend under extrusion. From Table II, it can be noted that the pressure drop at the extrusion head inlet for BD01 was 97 kPa, while for BD05 it was 1,096 kPa. The high residence time can have caused the blends components to degradate, especially PBT matrix, which is the main responsible for improving the impact strength of the blend. However, from Figure 5(d) and Table III it can be seen that the blend processed with the longer extrusion die has presented a lower DBTT, suggesting that the

higher residence time could have enhanced dispersion and distribution of the ABS disperse phase within PBT matrix.

The influence of the type of kneading blocks on the impact strength of the PBT/ABS blends is illustrated in Figure 5(e). The narrower kneading blocks (BD06), KB45/5/14, have improved the blend impact strength, while the DBTT has decreased, although the effect on the DBTT was more evident. Sample BD01, compounded with the 4KB45/5/42 screw presented a DBTT of −35°C, while sample BD06, blended with the 4KB45/5/14 screw, exhibited a DBTT of −50°C. A better distributive mixing, achieved with the kneading blocks KB45/5/14, is possibly the cause for it, since better distribution results in shorter distances among ABS disperse phase particles.

Figure 6 shows the curves of impact strength versus temperature for extruded and injection molded samples, and Table III presents impact strength at 20°C and DBTT of extruded and injection molded PBT/ABS blends. The curves present similar shapes, although the values of impact strength at 20°C and DBTT are different. Extruded samples tend to have superior impact strength than the respective samples injection molded after extrusion. The poorer impact strength observed for the injection molded samples can be attributed to the severe molecular orientation and to the fast freezing of the material taking place on the mold surface. Morphological changes, affecting PBT's crystallinity degree, can also have occurred. These considerations can imply in injection molding sample more brittle, as reflected by the smaller values of notched Izod impact strength. Meanwhile, the shearing rates involved in extrusion are smaller than the ones in injection molding, reducing the molecular orientation and improving the impact strength.

Another important fact is that the extruded samples have been submitted to only one processing step, and this would not lead to modifications on the crystalline structure, what could happen if PBT degradation had occurred. Nevertheless, the notched Izod impact strength versus temperature curves of all six PBT/ABS samples present roughly the same general shape, and the differences would be dependant exclusively on the processing method, that is, extrusion or injection molding after extrusion.

All six extruded PBT/ABS blends present higher tensile strength at break than the injection molded ones, as shown in Figure 7(a). This property depends only on the tensile stress versus tensile strain curve and since the injection molding samples are usually more oriented, the elongation would be smaller and the strength higher. However, the molecular chains of the extruded blends could be more relaxed after the extrusion process and the polymeric chains would get oriented during the tensile
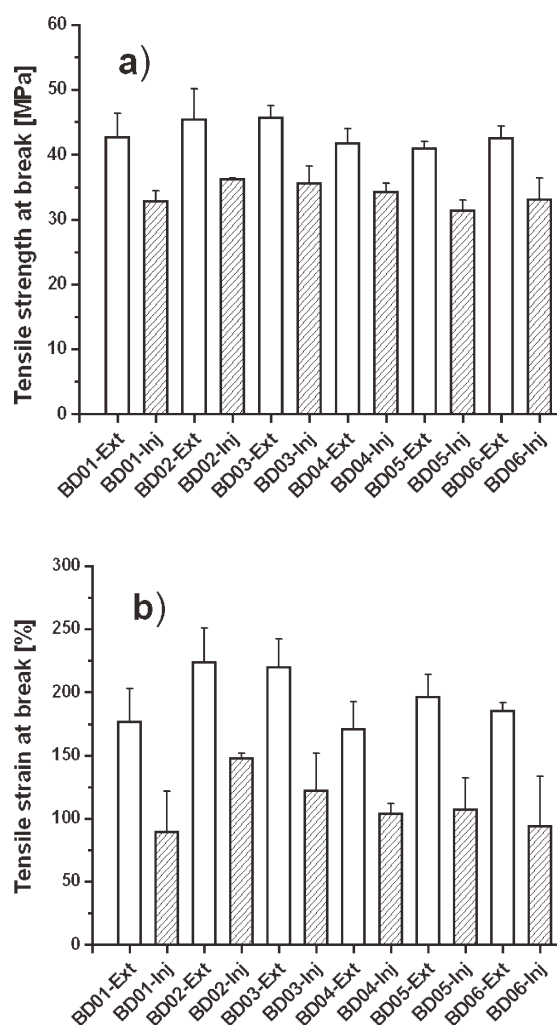
Figure 7 Graphs comparing the tensile stress properties of extruded (BD0i-Ext) and injection molded (BD0i-Inj) PBT/ABS blends. (a) Tensile strength at break and (b) tensile strain at break.

stress test, increasing the tensile strength of the blend. Figure 7(b) points out significant differences between the properties resulted of each transforma-

tion process. For the extruded blends, the average elongation at break is 200% and for the injection-molded ones, it is 100%. To explain the poorer values of tensile strength and strain at break of the injection molding samples, the degradation of the blends constituents has also to be taken into account. It could modify the crystalline morphology of PBT, making it less ductile. Therefore, tensile stress properties of samples obtained by distinct transformation processes, extrusion and injection molding, have revealed to be different.

PBT/ABS blends thermal behavior

Table IV shows the melting temperatures (T_{m1} and T_{m2}), the heats or enthalpies of fusion ($\Delta H1$ and $\Delta H2$), the T_c and the enthalpy of crystallization (ΔH_c) obtained by DSC. The first heat provides information about the influence of the processing parameters on the thermal behavior of the blends, while the second heat reveals the intrinsic thermal behavior of the blend, which has been cooled at $-10°C/$ min under nitrogen atmosphere. Thus, the second heat could be really useful to verify structural modifications due to the transformation processes. By analyzing the first heat, it can be said that the enthalpies of fusion of the injection molded samples showed to be high to the enthalpies of fusion of the extruded samples, indicating that the first samples had a higher crystallinity degree than the respective latter samples. Once more, degradation due to the injection molding process could be the responsible, because PBT molecular chains presenting lower molecular weight could easily diffuse in the melt material, arranging themselves into more perfect and larger crystalline structures. It should be emphasized, however, that the first heat still contains thermal and shearing backgrounds.

PBT's crystallization during cooling of the PBT/ABS blend has indicated that T_c and ΔH_c are higher

TABLE IV
Thermal Properties of the PBT/ABS Blends Analyzed by DSC

Sample	Process	First heating		Cooling		Second heating	
		T_{m1} (°C)	$\Delta Hm1$ (J/g)	T_c (°C)	ΔH_c (J/g)	T_{m2} (°C)	$\Delta Hm2$ (J/g)
BD01	Extrusion	228.8	36.2	187.5	−42.3	228.7	43.6
	Injection Molding	223.4	43.9	193.6	−54.2	223.0	54.7
BD02	Extrusion	226.0	48.5	189.6	−55.3	225.9	54.7
	Injection Molding	225.1	52.3	191.5	−60.5	224.8	60.8
BD03	Extrusion	225.2	51.2	187.9	−58.2	225.1	58.6
	Injection Molding	224.6	51.9	189.7	−59.2	224.6	59.2
BD04	Extrusion	225.8	43.6	191.1	−49.2	225.9	49.2
	Injection Molding	225.9	41.2	192.7	−51.7	224.5	52.7
BD05	Extrusion	226.7	42.9	189.8	−46.9	226.5	47.3
	Injection Molding	226.2	43.8	191.4	−48.5	224.9	49.1
BD06	Extrusion	225.4	42.4	185.8	−48.6	226.1	47.0
	Injection Molding	225.7	44.0	188.5	−52.8	225.3	50.4

in the injection molded samples than in the extruded samples. Second heat enthalpies of fusion were higher than first heat ones, probably due to the fact that the cooling rates used on the DSC analyses were far smaller than the cooling rates verified in extrusion and injection molding processes. The considerations made about PBT degradation during first heat also apply to the second heat. For all the six pairs of samples evaluated, the enthalpy of fusion and consequently the crystallinity degree have been always higher for the injection-molded samples, in comparison to the extruded samples. The same applies to the melting temperature.

The compatibilizing agent reduces the enthalpy of fusion of the compatibilized blends, as can be noted comparing the extruded binary blend BD02 and the compatibilized blends, processed with feed rate of 7.0 kg/h. The measured cooling and heating enthalpies were calculated only for the PBT amounts in the blends.

Using DSC and X-ray diffraction analyses, Tomar et al.[29] also observed a reduction in the crystallinity of PBT, when it was compatibilized with the acrylonitrile–styrene–butyl acrylate (ABAS) terpolymer, yet the addition of ABAS improved thermal stability of the blend. Nevertheless, comparing extruded and injection molded samples it is also clear that sample BD02 has its enthalpy of fusion increased from 54.7 J/g, extruded sample, to 60.8 J/g, injection molded sample. This confirms that PBT degradated during the injection molding process.

The differences in mechanical properties of extruded and injection molded samples, observed in Figures 6 and 7 are characteristic of the transformation process to which the blend has been submitted before the mechanical tests. As the mechanical properties (tensile stress and impact strength) exhibit exactly the same trends in extruded and injection-molded samples, as a function of the processing parameters, it is likely that the mixing process in an ICTSE defines the mechanical behavior of the blend.

CONCLUSIONS

The main conclusions achieved with this study are pointed out as follows.

- The flow simulation of the molten PBT/ABS blend was necessary to project the extrusion head and the extrusion dies. A flow following the power-law relation has been assumed and measurements obtained by capillary rheometry have been used in the calculations. The pressure drop monitored during the extrusions and the simulated values, for a 62.0 mm long extrusion die presenting parallel plates geometry and dimensions of 25.0 mm × 3.6 mm, are in good

agreement, proving that the simulation was efficient. The methodology developed has enabled the monitoring and control of operational parameters, such as, motor torque, molten temperature and pressure; and the manufacture of extruded ribbons with dimensions sufficient to perform tensile stress and Izod impact strength tests.
- The compatibilizing agent, MGE, has decreased the DBTT from 5°C to −35°C. However, the notched Izod impact strength has also been diminished. Regarding the extrusion processing parameters, it has been observed that higher feed rate, slower screw speed and narrower kneading blocks (KB45/5/14) have decreased the DBTT of the PBT/ABS blend. This suggests that the conditions above described have improved toughening mechanism, have preserved the chemical integrity of blend constituents, and have enhanced dispersion and distribution of ABS disperse phase within the PBT matrix.
- The mechanical properties of the extruded ribbons, processed with different process parameters, have exhibited the same trends of the samples injection molded after extrusion. The latter samples have presented poorer Izod impact strength, tensile strain at break and tensile strength at break than the respective extruded samples. Higher levels of molecular orientation, typical of the injection molding process, and PBT degradation during injection molding could be the causes for the loss in mechanical properties of the injection-molded blends.
- DSC thermograms of extruded and injection molded samples have revealed that the enthalpy of fusion of the injected samples was higher than the heat of fusion of the respective extruded blends, implying in higher crystallinity degree in the injection molded blends. This effect has been attributed to PBT degradation, which could have reduced PBT's melt viscosity, facilitating the displacement of the molecular chains within the blend and favoring the development of crystalline structures.

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